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Neutron Diffraction Study of Magnesium Deuteride*

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A magnesium deuteride preparation of composition $Mg(D_{0\cdot9}H_{0\cdot1})_2$ is found to be tetragonal with $a=4\cdot5025$, $c=3\cdot0123$ Å. The atomic positions are:

$$2\ \mathrm{Mg\ in}\ (000)\ (\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}),\ 4(\mathrm{D}+\mathrm{H})\ \mathrm{in} \pm\ (xx0)\ (\tfrac{1}{2}+x,\ \tfrac{1}{2}-x,\ \tfrac{1}{2})\ \mathrm{with}\ x=0\cdot306\pm0\cdot003.$$

The bond lengths are Mg–6D $=1\cdot95\pm0\cdot02$ Å. The structure is of the rutile type.

Some years ago it was shown by X-ray diffraction (Ellinger *et al.*, 1955) that magnesium hydride is tetragonal with two molecules in a unit cell of dimensions $a=4\cdot5618\pm0\cdot0005$, $c=3\cdot0205\pm0\cdot0005$ Å.

The two magnesium atoms were found to be in positions $(0, 0, 0)(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. It was suggested that the hydrogen atoms were located at the sites

$$\pm(x, x, 0)(\tfrac{1}{2}+x, \tfrac{1}{2}-x, \tfrac{1}{2})$$

with $x\approx0\cdot306$, *i.e.* that MgH_2 has the rutile type of structure. However, the hydrogen atoms had no measurable effect on the diffraction intensities, and accordingly there was no experimental proof for the proposed hydrogen positions. A direct determination of the hydrogen sites by means of neutron diffraction was therefore undertaken, using the deuteride in preference to the hydride.

Magnesium deuteride was prepared by reaction of deuterium gas with magnesium metal (obtained by decomposition of MgH_2) for four days at 510 °C.

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under a pressure of 270 atmospheres. The chemical analysis of the product was

$$\mathrm{MgD_2}\ 87{\cdot}8,\ \mathrm{MgO}\ 7{\cdot}0,\ \mathrm{Mg}\mathit{Me}\ 5{\cdot}2\%\,.$$

However, a contamination of 9·6 at.% hydrogen was found in the deuterium gas. It is believed that the hydrogen impurity comes from the walls of the stainless steel vessel in which the reaction was carried out. The same vessel had been used previously for magnesium hydride studies, and apparently had not been outgassed at sufficiently high temperature for sufficiently long time.

Table 1. *Neutron diffraction data for* MgD_2

HKL	$\sin^2\theta$ calc.	$\sin^2\theta$ obs.	Intensity calc.	Intensity obs.
110	0·0292	0·0292	21·2	15·2
101	0·0472	0·0476	1·5	1·8
200	0·0584	0·0613	1·9	44·5
111	0·0618		38·4	
210	0·0730	0·0724	14·8	15·1
211	0·1056	0·1050	29·6	28·0
220	0·1168	0·1164	12·9	12·5
002	0·1305	0·1307	10·6	13·7*
310	0·1460	0·1479	0·6	3·8
221	0·1494		2·7	
112	0·1597	0·1627	5·3	30·7
301	0·1640		25·9	
311	0·1786	0·1785	5·4	5·7
202	0·1889	0·1879	0·9	2·3
320	0·1898		1·2	
212	0·2035	0·2018	7·4	9·1†
321	0·2224	0·2248	0·5	1·1
400	0·2336	0·2347	1·8	1·6
222	0·2473	0·2480	8·5	15·7
410	0·2482		6·3	
330	0·2628	0·2640	5·1	5·0

* Coincidence with MgO(220).
† Coincidence with MgO(222).

Mr F. H. Ellinger made an X-ray diffraction pattern of the deuteride preparation and found the following unit cell dimensions:

$$a=4{\cdot}5025\pm0{\cdot}0005,\quad c=3{\cdot}0123\pm0{\cdot}0005\ \text{Å}\,.$$

The neutron diffraction pattern was obtained at the Argonne National Laboratory using a cylindrical sample and a neutron beam of wavelength 1·088 Å. In the range below $2\theta=62°$ the pattern shows sixteen diffraction peaks the positions and intensities of which could be measured with reasonable precision, and the results of the measurements for these lines are listed in Table 1. Because of excessive overlap between neighboring diffraction peaks it was not possible to get reliable intensity data for $2\theta>62°$.

As shown in Table 1 all diffraction lines in the pattern correspond to the tetragonal unit cell for MgD_2 found from X-ray data. Reflections for which $H+K+L$ is odd are due to the deuterium atoms only, and these reflections were not observable in the X-ray patterns.

Diffraction lines due to the magnesium metal impurity were not observable, and the strongest diffraction lines of the MgO impurity are hidden under large superimposed diffraction peaks of MgD_2.

The accepted values for the coherent neutron scattering powers, *b*, of the various nuclei are (Hughes & Harvey, 1955):

Nucleus	*b*
H	$-0{\cdot}38\times10^{-12}$
D	0·65
Mg	0·54

When allowance is made for the hydrogen impurity, the effective scattering power for deuterium in the sample becomes $b=0{\cdot}55\times10^{-12}$.

The expression for the calculated intensity, I_c, is

$$I_c \propto |F_H|^2 j \exp\,(-2M)/\sin^2\theta\cos\theta \qquad (1)$$

where j is the multiplicity factor, and $M=B\sin^2\theta/\lambda^2$ with B the overall isotropic temperature factor for the compound.

Simple consideration of the experimental intensities given in Table 1 show that MgD_2 does, indeed, have the rutile type of structure as previously suggested, *i.e.*: 2Mg in $(0,0,0)(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, 4D in $\pm(x,x,0)(\frac{1}{2}+x,\frac{1}{2}-x,\frac{1}{2})$.

The best agreement between observed and calculated intensities is obtained for the following values of the adjustable parameters:

$$x=0{\cdot}306\pm0{\cdot}003,\quad B=2{\cdot}0\pm0{\cdot}5\ \text{Å}^2.$$

Each magnesium atom is bonded to six deuterium atoms, the bond lengths being 1·95 ± 0·02 Å. The closest D–D separation is 2·47 ± 0·03 Å.

On the assumption of ionic binding and an ionic radius of 0·64 Å for Mg^{2+} one finds a radius of 1·31 Å for the D^- ion. A slightly larger radius of 1·35 Å for D^- is observed in LiD (Zintl & Harder, 1935).

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